Electronic structure of alkali metal-doped M_8Si_{46} (M=Na, K) clathrates

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INTRODUCTION

Silicon clathrates are networks of Si cages and can be considered as the Si-analog to fullerenes (C_{60}) with Silicon substituting the Carbon. The Si cages in clathrate structures share faces to satisfy the sp^3 bonding. All Si-atoms in clathrates are tetrahedrally coordinated with the Si-atoms occupying the centers of slightly imperfect tetrahedrons. Their indirect bandgap makes silicon clathrates promising candidates for optoelectronical and thermoelectrical devices. It has been shown recently that semiconductor clathrates also have thermoelectric properties [6] and can form three-dimensional arrays of nano-sized clusters [7]. Although pure silicon and germanium clathrates are predicted to be locally stable, experiments have been able to synthesize the metal-doped clathrate compounds only. The interaction between the metallic impurity atoms inside the clathrate and the semiconductor skeleton modifies the electronic structure of the clathrates. A charge-balanced Zintl-phase model has been suggested for these compounds with the guest (alkali metal or alkaline earth) donating its charge to the host frame. This model was confirmed by band structure calculations of Na_8Si_{46} [8], K_8Ge_{46} [9] and $Na_2Ba_6Si_{46}$ [10]. Recent experiments however, have raised the question whether the guest is close to being neutral in some cases [11-12]. In order to estimate the validity of the rigid band model, we have carried out x-ray emission measurements of crystalline Si (c-Si), K_8Si_{46} and Na_8Si_{46} and compare these to our calculations.

DISCUSSION OF CALCULATIONS AND MEASUREMENTS

The densities of (occupied electronic) states (DOS) of Si_{46}, Na_8Si_{46} and K_8Si_{46} obtained from FLAPW calculations are shown in Fig. 1. The main features of total and partial density of states (DOS) are very similar for all three compounds. Differences occur mainly in the degree of filling of the energy bands by valence electrons and the energy position with respect to the Fermi level. For Si_{46} the valence band is completely filled and the conduction band is empty giving rise to its insulating or intrinsic semiconducting behavior. In the cases of Na_8Si_{46} and K_8Si_{46} the additional sodium and potassium electrons fill the next energy band and the Fermi level is overlapping the conduction band providing the metallic properties of this doped clathrate. Similar behavior has been observed in calculated band structures of Ge_{46} and K_8Ge_{46} and Na_8Si_{46} and Ba_8Si_{46}. The conduction-band density of states does not show strong modifications upon the inclusion of metal atoms. This is due to weak hybridization between the Si_{46} conduction-band states and Na and K states and indicates that metal-metal and metal-Si interactions are ionic and that Na and K act as electron donors. Therefore alkali metal doping introduces a narrow band labeled as *D* in Fig. 1. This band - directly below the Fermi level - is separated by an energy gap of several eV from the main density of electronic states (features A, B and C) and should give rise to a spectroscopically observable feature. Its origin is in the lowest conduction band in the undoped Si_{46} clathrate. Our calculations also indicate that a significant charge transfer from Na or K to the Si skeleton is taking place and the rigid band model is a valid model for describing the electronic structure of these clathrates. We define the rigid band as a rigid shift of the Fermi level from the pristine Si_{46} to Na_8Si_{46} when filling empty bands with electrons from the Na atom.

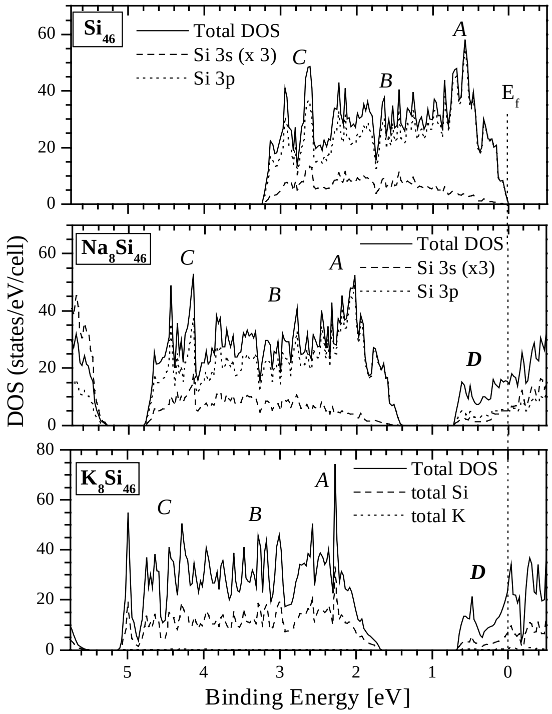

Figure 1. Total and partial density of states (DOS) for Si_{46} and clathrates Na_8Si_{46} and K_8Si_{46}.

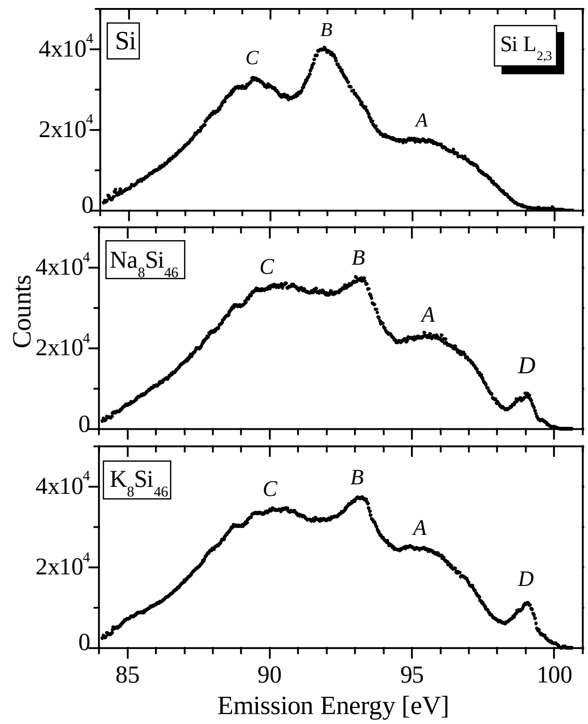

Figure 2. Si $L_{2,3}$ XES of c-Si, Na_8Si_{46} and K_8Si_{46}.

Fig. 2 displays the Si $L_{2,3}$ emission spectra of crystalline silicon (c-Si) and Si-clathrates (Na_8Si_{46} and K_8Si_{46}) as solid dots. Three main features labeled *A*, *B* and *C* are observed in both, crystalline Si and clathrates and are due to transitions from *s, d* and *sd*-like bands, respectively. The feature *D* discussed above has its spectroscopic counterpart in the additional feature that is present at 99 eV and labeled *D*. Feature D is present only in the spectra clathrates. It results from transitions of the lowest conduction band, introduced due to charge-transfer from the metal atoms and it corresponds to feature *D* in Fig. 1. The spectroscopic presence of this band demonstrates good agreement between experiment and density of state calculations and that the rigid band model is a good description for these materials.

This work was supported by Natural Sciences and Engineering Research Council (NSERC), the Russian Foundation for Basic Research (Projects 00-15-96575) and the NATO Collaborative Linkage Grant.

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